# First Pressure Derivatives of Polycrystalline Elastic Moduli: Their Relation to Single-Crystal Acoustic Data and Thermodynamic Relations

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This paper demonstrates that, for a given crystalline solid, the first pressure derivatives of polycrystalline elastic moduli can be predicted either from the corresponding derivatives of anisotropic single-crystal elastic constants or from their single-crystal third-order elastic constants. Theoretical relations for the isotropic polycrystalline acoustic data in terms of their single-crystal acoustic data are presented here for cubic, hexagonal, trigonal, and tetragonal crystals; these have been successfully applied for four cubic solids (Al, Cu,  $\alpha$ -Fe, and MgO) and one hexagonal metal (Mg). It is shown for these solids that the calculated isotropic acoustic data agree essentially with experimental acoustic data determined on their polycrystalline specimens, thus establishing the validity of the theoretical relations. It is concluded that the acoustic data measured on *fully dense* polycrystalline specimens may be as useful as the single-crystal acoustic data in the study of the equation of state of solids, for example. And further, when anisotropic single-crystal acoustic data are available, these can be converted into isotropic polycrystalline acoustic data so that in their applications, the use of the acoustic data becomes more practical.

#### 1. INTRODUCTION

The first pressure derivatives of the second-order elastic constants of a solid provide an important source of information for studies of lattice dynamics and of the general equation of state of the solid. However, measurements of these quantities are frequently limited by the unavailability of single-crystal specimens large enough for acoustic measurements to be made upon them. On the other hand, the fabrication of fully dense polycrystalline specimens has been possible in recent years for a number of materials, including metals, oxides, fluorides, sulfides (like  $\beta$ -ZnS), selenides (like ZnSe), and tellurides (like CdTe) as well as a large number of intermetallic compounds (like  $\beta$ -SiC and TiB<sub>2</sub>). Acoustic measurements on polycrystalline specimens also are simpler in principle and of more practical use than those on single-crystal specimens, because the acoustic properties of polycrystals are isotropic, whereas those of single-crystals are anisotropic. Furthermore, for a polycrystalline specimen, measurements of only two sound velocities (one longitudinal and one transverse) as a function of hydrostatic pressure suffice to give the complete description of the second-order deformation behavior of the solid under hydrostatic pressure. The question then arises whether the acoustic data (e.g., the second-order elastic constants and their pressure derivatives) determined on polycrystalline specimens are equivalent to the corresponding quantities measured on single crystals. The primary purpose of this paper is to examine this question by computing, on the basis of a theoretical scheme,<sup>1</sup> polycrystalline

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M.I.T., Cambridge, Mass. <sup>1</sup> (a) D. H. Chung, Proc. 4th Technical Society of Engineering Science, paper No. 5 (1966); (b) R. Hill, Proc. Phys. Soc. (London) 65, 349 (1952). It is noted that Ref. 1a discusses the validity of the Voigt-Reuss-Hill approximation and its relation to other theoretical schemes of averaging the single-crystal elastic constants for a polycrystalline behavior. Other theoretical schemes referred here include a self-consistent method of Kröner (1958) and a variational method due to Hashin and Shtrikman (1962).

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acoustic data from the corresponding single-crystal data, and comparing the result with experimentally determined values.

In the section immediately following, theoretical relations are presented for the first pressure derivatives of polycrystalline elastic moduli in terms of their singlecrystal elastic constants and pressure derivatives for cubic, hexagonal, trigonal, and tetragonal crystals. Then, in Sec. 3, Sec. 2 is applied for four cubic solids and one hexagonal metal, since for these solids both the single-crystal and polycrystalline acoustic data are found in the literature. And, then in Sec. 4, the present work with cubic crystals is explicitly discussed for three thermodynamic boundary conditions (adiabatic, isothermal, and mixed). In Sec. 5, a procedure to calculate polycrystalline acoustic data from the single-crystal third-order elastic constants is presented for cubic crystals. And, finally in Sec. 6, the present work is discussed and its implications and possible applications in solid-state studies are indicated in brief.

#### RELATIONSHIP BETWEEN 2. THE FIRST PRESSURE DERIVATIVES OF THE SINGLE-CRYSTAL ELASTIC CONSTANTS AND THOSE OF POLYCRYSTALLINE ELASTIC MODULI

The first pressure derivatives of polycrystalline elastic moduli in terms of the corresponding derivatives of the single-crystal elastic constants can be given as:

For the bulk modulus K,

$$dK^*/dp = \frac{1}{2}(dK_V/dp + dK_R/dp), \qquad (1)$$

and for the shear modulus G,

$$dG^{*}/dp = \frac{1}{2}(dG_{V}/dp + dG_{R}/dp).$$
 (2)

$$dK_V/dp = f_1(dc_{\mu\nu}/dp) \tag{3a}$$

$$dK_R/dp = f_2(dc_{\mu\nu}/dp), \qquad (3b)$$

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 $dG_R/dp = \frac{4}{5}(G_R/C_a)^2(dC_a/dp) + \frac{3}{5}(G_R/c_{44})^2(dc_{44}/dp),$ 

 $C_a = (c_{11} - c_{12})$ 

 $G_R = (5C_a c_{44}) / (3C_a + 4c_{44}).$ 

 $dK_V/dp = \frac{1}{9} \left[ 2(dc_{11}/dp + dc_{12}/dp) + dc_{33}/dp + 4(dc/dp) \right],$ 

 $K_R = C_c/C_b$ 

 $dK_R/dp = C_b(K_R/C_c)^2(dC_c/dp) - (K_R^2/C_c)(dC_b/dp),$ 

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(4a) $dG_V/dp = f_3(dc_{\mu\nu}/dp)$ 

(4b)  $dG_R/dp = f_4(dc_{\mu\nu}/dp);$ 

where  $f_1$  through  $f_4$  are some linear combinations of the

(a) Cubic Crystals:

 $dK_V/dp = dK_R/dp = dK^*/dp = dc_{11}/dp - \frac{2}{3}(dC_a/dp),$ (5)(6) $dG_V/dp = \frac{1}{5}(dC_a/dp) + \frac{3}{5}(dc_{44}/dp),$ 

each heading.

single-crystal elastic constants and their pressure de-

rivatives, and they depend upon the crystal symmetry.

The rigorous expressions for Eqs. (3) and (4) depend, therefore, on the symmetry of crystal in question; in

the following, the expressions for cubic, hexagonal,

trigonal, and tetragonal crystals are presented under

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(b) Hexagonal Crystals:

and where

where

and

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 $dG_R/dp = \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + 2(G_R/C_a)^2 (dC_a/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c)^2 (dC_c/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c) (dK_V/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c) (dK_V/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c) (dK_V/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c) (dK_V/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c) (dK_V/dp) - 6(G_R^2/C_c) (dK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (G_R/C_c) (GK_V/dp) - 6(G_R^2/C_c) (GK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (GK_V/dp) - 6(GK_V/dp) + \frac{1}{5} \left[ \frac{6K_V (GK_V/dp) - 6(GK_V/dp) + \frac{1}{5} \left$  $+2(G_R/c_{44})^2(dc_{44}/dp)+(G_R/c_{66})^2(dc_{66}/dp)],$ (12)where (13) $K_{v} = \frac{1}{9} \left[ 2(c_{11} + c_{12}) + c_{33} + 4c_{13} \right],$ and (14) $G_R = \frac{5}{2} \left[ C_d / C_e \right],$ where  $C_d = C_c c_{44} c_{66}$ and

 $dK_R/dp = \text{Eq.}(9),$ 

and

where

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(3a)

(3b)

 $C_b = c_{11} + c_{12} + 2c_{33} - 4c_{13}$  $C_c = c_{33}(c_{11} + c_{12}) - 2c_{13}^2$ .  $dG_V/dp = (1/30) [dC_b/dp + 12(dc_{44}/dp) + 12(dc_{66}/dp)],$  $C_e = C_c(c_{44} + c_{66}) + 3K_V c_{44} c_{66}.$  $dK_V/dp = \text{Eq.}(8),$ 

(c) Trigonal Crystals:

 $dG_V/dp = \text{Eq.} (11).$  $dG_R/dp = \frac{2}{5}(G_R/C_h)^2 [(C_a + 2c_{44})dC_h/dp] - \frac{2}{5}(G_R^2/C_h)[dC_a/dp + 2(dc_{44}/dp)]$ 

(18) $+ \frac{6}{5} \left[ K_V (G_R/C_c)^2 (dC_c/dp) - (G_R/C_c) (dK_V/dp) \right],$ 

(19) $G_R = \frac{5}{2} \left[ C_f / C_g \right],$ 

 $C_{1} = C_{c}(c_{44}c_{66} - c_{14}^{2})$  $C_{a} = C_{c}(c_{44} + c_{66}) + 3K_{V}(c_{44}c_{66} - c_{14}^{2}),$  and

$$C_h = C_a c_{44} - 2c_{14}^2.$$

 $K_V$  is given by Eq. (13) and its first pressure derivative is given by Eq. (8) and

$$dC_h/dp = C_a(dc_{44}/dp) + c_{44}(dC_a/dp) - 4c_{14}(dc_{14}/dp).$$

(d) Tetragonal Crystals:

$$dK_V/dp = \text{Eq. (8)}, \tag{20}$$

and

$$dK_R/dp = \text{Eq. (9)}.$$

$$dG_V/dp = \frac{1}{80} \left[ 3(dC_a/dp) + 12(dc_{44}/dp) + 6(dc_{66}/dp) + dC_b/dp \right],$$
(22)

where

$$dC_b/dp = dc_{11}/dp + dc_{12}/dp + 2(dc_{33}/dp) - 4(dc_{13}/dp)$$

and

 $dC_a/dp = dc_{11}/dp - dc_{12}/dp.$ 

$$dG_R/dp = \frac{1}{5} \left[ 2(G_R/C_a)^2 (dC_a/dp) - 6(G_R/C_c)^2 (dK_V/dp) + 6K_V (G_R/C_c)^2 (dC_c/dp) \right]$$

 $+2(G_R/c_{44})^2(dc_{44}/dp) + (G_R/c_{66})^2(dc_{66}/dp)],$  (23)

(24)

where

where

 $C_i = 5C_a C_c c_{44} c_{66},$ 

and

 $C_{j} = [2C_{c}c_{44}c_{66} + 6K_{V}C_{a}c_{44}c_{66} + C_{a}C_{c}c_{44} + 2C_{a}C_{c}c_{66}].$ 

 $G_R = C_i/C_i$ 

 $K_V$  and its first pressure derivative are given by Eqs. (13) and (8), respectively, and

 $dC_c/dp = (c_{11}+c_{12})(dc_{33}/dp) + c_{33}(dc_{11}/dp + dc_{12}/dp) - 4c_{13}(dc_{13}/dp).$ 

## 3. COMPARISON OF THE PREDICTED ISOTROPIC ACOUSTIC DATA WITH EXPERIMENTAL POLYCRYSTALLINE ACOUSTIC DATA

Having presented theoretical expressions for isotropic (polycrystalline) acoustic data in terms of anisotropic (single-crystal) acoustic data, we proceed in this section to compare the computed values of the isotropic acoustic data with experimental polycrystalline acoustic data. Comparison is made here for crystalline Al, Cu,  $\alpha$ -Fe, MgO, and Mg, since for these solids, results on ultrasonic-pressure experiments are reported in the literature individually for both single-crystal and polycrystalline materials.

3.1. Cubic Crystals

Table I lists values of the first pressure derivatives of single-crystal elastic constants for Al,<sup>2,3</sup> Cu,<sup>2,4,5</sup>  $\alpha$ -Fe,<sup>6</sup> and MgO.<sup>7</sup> The values listed under  $(\partial c_{\mu\nu}s/\partial p)_T$  are the experimental quantities resulting from the usual ultrasonic-pressure experiments. Other quantities entered are computed results according to thermodynamic relations to be presented in Sec. 4, and they are discussed there. Using the values of  $c_{\mu\nu}^{s}$  and  $(\partial c_{\mu\nu}^{s}/\partial p)_{T}$ , the isotropic values of  $(\partial B^{*s}/\partial p)_T$  and  $(\partial G^*/\partial p)_T$  are computed according to the relations given in the preceding section, and these are compared with experimental polycrystalline acoustic data in Table II. Here the quantity  $(\partial L^{*s}/\partial p)_T$  is the isothermal pressure derivative of adiabatic longitudinal modulus calculated from  $(\partial B^{**}/\partial p)_T$  and  $(\partial G^*/\partial p)_T$  in the usual way (i.e.,  $L^* = K^* + 4G^*/3$ ). The polycrystalline acoustic data entered in Table II are those compiled by Birch<sup>8</sup> and also by Voronov and Vereshchagin.9 Note that for every solid, the values of the pressure derivatives for the bulk, shear, and longitudinal moduli calculated from the single-crystal acoustic data are in essential agreement with the corresponding values measured on actual polycrystalline specimens. The observed discrepancies between the predicted and measured values for the pressure derivatives of isotropic elastic moduli are always within the scatter in both the single-crystal and polycrystalline acoustic data themselves. The kind of agreement seen here lends support to the validity of the theoretical relations presented in Sec. 2.

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<sup>&</sup>lt;sup>2</sup> D. Lazarus, Phys. Rev. 76, 545 (1949).

<sup>&</sup>lt;sup>3</sup> R. E. Schmunk and C. S. Smith, J. Phys. Chem. Solids 9, 100 (1959).

<sup>&</sup>lt;sup>4</sup> W. B. Daneils and C. S. Smith, Phys. Rev. 111, 713 (1958).
<sup>5</sup> Y. Hiki and A. V. Granato, Phys. Rev. 144, 411 (1966).
<sup>6</sup> C. A. Rotter and C. S. Smith, J. Phys. Chem. Solids 27, 267 (1966).

<sup>&</sup>lt;sup>7</sup> E. H. Bogardus, J. Appl. Phys. 36, 2504 (1965).

<sup>&</sup>lt;sup>8</sup> F. Birch, *Handbook of Physical Constants* S. P. Clark, Jr., Ed. (Geological Society of America, Inc., New York, 1966), Memoir No. 97, p. 124.

<sup>&</sup>lt;sup>9</sup> F. F. Voronov and L. F. Vereshchagin, Fiz. Metal Metalloved 11, 443 (1961).

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## 3.2. Hexagonal Crystals

In the literature, experimental acoustic data on both single-crystal and polycrystalline materials of Mg are reported. The single-crystal acoustic data are due to Schmunk and Smith<sup>3</sup>; for polycrystalline data, we use the acoustic data reported by Voronov and Vereshchagin.9 Table III summarizes the single-crystal acoustic data. In Table IV, we compare the isotropic acoustic data resulting from the present calculations with the corresponding values measured on polycrystalline specimens. The agreement is good as may be seen from the table.

## 4. THERMODYNAMIC RELATIONS FOR THE ADIABATIC AND ISOTHERMAL ACOUSTIC DATA

Typical ultrasonic experiments, in which pressure is a variable, involve measurements of the behavior of an elastic wave propagating in a statically stressed crystal. Thermodynamically, the ultrasonic velocity measurements in the crystal (specimen) involve an adiabatic process: on the other hand, the application of pressure to the specimen is an isothermal process. Thus, the acoustic data resulting from such experiments are neither thermodynamically "pure" adiabatic nor thermodynamically "pure" isothermal quantities, but are "mixed" quantities. How, then, can one calculate (a) isothermal pressure derivatives of the isothermal elastic moduli and (b) adiabatic pressure derivatives of the adiabatic elastic moduli from the experimentally determined isothermal pressure derivatives of the adiabatic elastic moduli? In the following discussion, the thermodynamic relations applicable for cubic crystals are presented for (a) and (b) in terms of the measured quantities resulting from the usual ultrasonic-pressure experiments.

At the absence of pressure, it is well-known that the relationships between the adiabatic and isothermal values of the second-order elastic constants are given by the following:

$$\begin{cases} c_{11}^{s} - c_{11}^{T} \\ c_{12}^{s} - c_{12}^{T} \\ K^{s} - K^{T} \end{cases} = \frac{T\beta^{2}}{\rho C_{p} (s_{11}^{s} + 2s_{12}^{s})^{2}} = T\beta \gamma_{G} K^{T}, \quad (25)$$

and

$$c_{44}{}^{s} = c_{44}{}^{T} = c_{44}. \tag{26}$$

Where  $\beta$  is the coefficient of volume expansion,  $\rho$  is the density, T is the temperature, and  $\gamma_G$  is the Grüneisen constant given by

$$\gamma_G = \beta K^s / \rho C_p = \beta V K^T / C_v = \beta V K^s / C_p.$$
(27)

The superscripts s and T denote the adiabatic and the isothermal values, respectively.  $C_p$  and  $C_v$  are the specific heats at constant pressure and that at constant volume, respectively, and the difference between them

TABLE I. Pressure derivatives of crystalline Al, Cu, 
$$\alpha$$
-Fe, and MgO at different thermodynamic boundary conditions ( $\sim 300^{2}$ K)

		dc11/dp			$dc_{12}/dp$		dc44/	$dp_{\prime}$		dK/dp	
<b>Material</b>	$(\partial c_{11}^{s}/\partial p)_T$	$(\partial c_{11}^{s}/\partial p)_{s}$	$(\partial c_{11}^T/\partial p)_T$	$(\partial c_{12}^{s}/\partial p)_{T}$	$(\partial c_{12}^{s}/\partial p)_{s}$	$(\partial c_{12}^T/\partial p)_T$	$(\partial c_{44}/\partial p)_T$	$(\partial c_{44}/\partial p)_s$	$(\partial K^*/\partial p)_T$	$(\partial K^s/\partial p)_s$	$(\partial K^T/\partial p)_T$
Al(49Ll)* Al(59Sl)b	8.40 7.38	8.02 7.00	8.83 7.71	1.80 4,14	1.58 3.92	2.23 4.47	2.10 2.31	1.99 2.20	3.95 5.22	3.69 4.94	4.37 5.55
Cu(49Ll) a	5.23	5.06	5.35	4.04	3.96	4.16	1.04	0.93	4.44	4.33	4.56
Cu(58Dl)°	6.37	6.20	6.42	5.21	5.13	5.26	2.36	2.24	5.39	5.48	5.65
Cu (66Hl) <sup>d</sup>	5.93	5.76	6.00	4.95	4.87	5.02	2.77	2.66	5.28	5.17	5.35
e-Fe(66R1)*	7.51	7.39	7.54	5.19	5.13	5.22	2.66	2.63	5.96	5.88	5.99
MgO(65Bl)f	8.90	8.74	8.94	1.76	1.78	1.80	1.19	1.16	4.14	4.10	4.18
<ul> <li>49LI: D. Lazarus,</li> <li>59SI: R. E. Schm</li> <li>58DI: W. B. Dan</li> </ul>	, Phys. Rev. 76, 54, unk and C. S. Smith iels and C. S. Smith	5 (1949). h, J. Phys. Che. 1, Phys. Rev. 11	m. Solids 9, 100 (11, 713 (1958).	(1959).		d 66H1: Y. Hiki e 66R1: C. A. Rot f 65B1: E. H. Bos	and A. V. Granat tter and C. S. Sm zardus. J. Appl. 1	o, Phys. Rev. 1 uith, J. Phys. Ch Phys. 36, 2504 (	44, 411 (1966). em. Solids 27, 26 1965).	57 (1966).	

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TABLE II. Comparison of predicted and experimental isotropic pressure derivatives of polycrystalline elastic moduli for Al, Cu,  $\alpha$ -Fe, and MgO ( $\sim$ 300°K).

			Is	othermal press	ure derivatives of	adiabatic moduli	
×,		reference <sup>a</sup>	(6	∂K*/∂p) <sub>T</sub>	$(\partial G^* / \partial p)_T$	$(\partial L^*/\partial p)_T$	
	Al	Calculated (49Ll)*	** · · · · · ·	3.95	2.71	7.56	
		Calculated (59Sl)		5.22	2.01	7.90	
		Measured (61Vl) <sup>b</sup>		4.75	2.00	7.42	
		Measured (66Bl)°		3.9	2.2	6.8	
						· · · ·	
	Cu	Calculated (49Ll)		4.44	0.86(?)	5.59(?)	
		Calculated (58Dl)		5.59	1.36	7.40	
		Calculated (66Hl)	1. S. M.	5.28	1.45	7.21	
		Measured (66 Bl)°		4.9	1.4	6.8	
	α-Fe	Calculated (66Rl)		5.96	1.91	8.50	
		Measured (61VI)b		5.13	2.16	8.01	
		Measured (66Bl)°		4.0	1.9	6.5	2 · · · ·
	MgO	Calculated (65Bl)		4.14	2.47	7.43	
	5	Measured (66Bl)°		3.9	2.6	7.4	

Therefore,

following.

yields

<sup>a</sup> See Table I for the complete reference.

<sup>b</sup> 61Vl: F. F. Voronov and L. F. Vereshchagin, Fiz. Metal Metalloved. 11, 443 (1961).

<sup>6</sup> 66Bl: F. Birch, Handbook of Physical Constants, S. P. Clark, Jr., Ed (Geological Society of America, 1966), Memoir 97, p. 124.

 $K^T = K^* A^{-1}$ 

and this is a convenient relation to be used in the

Differentiating Eq. (30), with respect to pressure,

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$$C_p - C_v = TV\beta^2 K^T = T\beta\gamma_G C_v. \tag{28}$$

It may be seen from Eqs. (25) and (28) that the two bulk moduli and the two specific heats have the same ratio:

$$K^{*}/K^{T} = C_{p}/C_{v} = 1 + TV\beta^{2}K^{*}/C_{p} = 1 + T\beta\gamma_{g} = A.$$
 (29)

$$(\partial K^{T}/\partial p)_{T} = (\partial K^{s}/\partial p)_{T} + [(A-1)/A][1 - (2/\beta K^{T})(\partial K^{T}/\partial T)_{p} - 2(\partial K^{s}/\partial p)_{T}] + [(A-1)/A]^{2}[(\partial K^{s}/\partial p)_{T} - (1/\beta^{2})(\partial \beta/\partial T)_{p} - 1].$$
(31)

The quantity  $(\partial K^T/\partial T)_p$  can be obtained from the experimental  $(\partial K^s/\partial T)_p$  by differentiating Eq. (30), with respect to temperature. Thus

$$(\partial K^T / \partial T)_p = (1/A) (\partial K^s / \partial T)_p - (K^T / A) (\partial A / \partial T)_p, \tag{32}$$

where

$$(\partial A/\partial T)_p = A[(A-1)/A]\{1/T + (1/\beta)(\partial\beta/\partial T)_p + (1/K^{\mathfrak{s}})(\partial K^{\mathfrak{s}}/\partial T)_p$$

 $+\beta [1+(1/\beta^2)(\partial\beta/\partial T)_p] - (1/C_p)(\partial C_p/\partial T)_p]. \quad (33)$ 

Equation (31) is the desired relation from which one can calculate the isothermal pressure derivative of the isothermal bulk modulus from the experimentally measured  $(\partial K^s/\partial p)_T$ , the isothermal pressure derivative of the adiabatic bulk modulus. Equation (31) was given first by Overton.<sup>10</sup> Equation (32) is the relation through which one can convert the isothermal temperature derivative of the isothermal bulk modulus from the experimental  $(\partial K^s/\partial T)_p$ , the isothermal temperature derivative of the adiabatic bulk modulus.

It can be shown that, although Eqs. (25) and (26) are referred to the zero-pressure condition, these relations hold also for all the other pressures. Differentiating Eq. (25), with respect to pressure, yields

$$(\partial c_{11}^T / \partial p)_T - (\partial c_{11}^s / \partial p)_T = (\partial c_{12}^T / \partial p)_T - (\partial c_{12}^s / \partial p)_T = (\partial K^T / \partial p)_T - (\partial K^s / \partial p)_T = B,$$
(34)

where an expression for B may be found from Eq. (31):

$$\frac{B = \left[ (A-1)/A \right] \left[ 1 - (2/\beta K^T) \left( \partial K^T/\partial T \right)_p - 2(\partial K^*/\partial p)_T \right] + \left[ (A-1)/A \right]^2 \left[ (\partial K^*/\partial p)_T - (1/\beta^2) \left( \partial \beta/\partial T \right)_p - 1 \right].$$
(35)

n, Jr., J. Chem. Phys. 37, 116 (1962)

Similarly, differentiating Eq. (26), with respect to pressure, yields

$$(\partial c_{44}{}^T/\partial p)_T = (\partial c_{44}{}^s/\partial p)_T = (\partial c_{44}/\partial p)_T.$$
(36)

Equations (34) and (36) are the desired expressions by which one finds the isothermal pressure derivatives of the isothermal elastic constants in terms of the experimentally measured  $(\partial c_{\mu\nu}^{s}/\partial p)_{T}$ , the isothermal pressure derivatives of the adiabatic elastic constants.

The adiabatic pressure derivatives of the adiabatic elastic constants can also be calculated from the experimentally measured isothermal pressure derivatives of the adiabatic elastic constants. Using the differential rule

$$(\partial/\partial p)_s = (\partial/\partial p)_T + (\partial/\partial T)_p (\partial T/\partial p)_s, \quad (37)$$

where

$$(\partial T/\partial p)_s = TV\beta/C_p = T\gamma_G/K^s = T\gamma_G\chi^s = C, \quad (38)$$

we find the relation<sup>11</sup>

$$(\partial c_{\mu\nu}{}^{s}/\partial p)_{s} = C(\partial c_{\mu\nu}{}^{s}/\partial T)_{p} + (\partial c_{\mu\nu}{}^{s}/\partial p)_{T}.$$
 (39)

Thus, for cubic crystals, Eq. (39) results in the following relations:

$$(\partial c_{11}^{s}/\partial p)_{s} = C(\partial c_{11}^{s}/\partial T)_{p} + (\partial c_{11}^{s}/\partial p)_{T}, \quad (40)$$

$$(\partial c_{12} / \partial p)_s = C (\partial c_{12} / \partial T)_p + (\partial c_{12} / \partial p)_T, \quad (41)$$

and

$$(\partial c_{44}^{s}/\partial p)_{s} = C(\partial c_{44}^{s}/\partial T)_{p} + (\partial c_{44}^{s}/\partial p)_{T}; \quad (42)$$

and, for the case with the bulk modulus,

$$(\partial K^{s}/\partial p)_{s} = C(\partial K^{s}/\partial T)_{p} + (\partial K^{s}/\partial p)_{T}.$$
 (43)

The thermodynamic relations given thus far are for the single-crystal elastic constants and their pressure derivatives. In terms of these relations, the corresponding thermodynamic relations for the polycrystalline values can be obtained.

The pressure derivative of the polycrystalline longitudinal modulus can be given in terms of Eqs. (1) and (2) as

$$(\partial L^*/\partial p)_T = (\partial K^*/\partial p)_T + \frac{4}{3}(\partial G^*/\partial p)_T, \quad (44)$$

or in terms of the single-crystal elastic constants and

Index for elastic constants	11	33	44	66	12	13
$\begin{array}{c} c_{\mu\nu} ^{*} (\times 10^{11} \\ \mathrm{dyn/cm^2}) \end{array}$	5.974	6.170	1.639	1.680	2.614	2.16
$(\partial c_{\mu\nu} * / \partial p)_T$	6.11	7.22	1.58	1.36	3.39	2.54

L	ABLE IV. Comparison	of predicted and	experimental	isotropic pressu	re derivatives of	polycrystallin	ie elastic moduli	for hexagonal	Mg.	
Isotropic	Darriter		dK/dp			dG/dp			dL/dp	
pressure derivatives	$(g/cm^3)$	$(\partial K_{V}/\partial p)_{T}$	$(\partial K_R/\partial p)_T$	$(\partial K^*/\partial p)_T$	$(\partial G_V/\partial p)_T$	$(\partial G_R/\partial p)_T$	$(\partial G^*/\partial p)_T$	$(\partial L_V/\partial p)_T$	$(\partial L_R/\partial p)_T$	$(\partial L^*/\partial p)_T$
Calculated (59Sl) <sup>a</sup>	1.738	4.06	4.06	4.06	1.63	1.61	1.62	6.24	6.20	6.22
Measured (61V1) <sup>b</sup>	1.731	• • •	/	4.18		:	1.53	:	:	6.22

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$$(\partial L^* / \partial p)_T = (\partial c_{11} / \partial p)_T - (8/15) [1 - (G_R / C_a)^2] \times (\partial C_a / \partial p)_T + \frac{2}{5} [1 + (G_R / c_{44})^2] (\partial c_{44} / \partial p)_T, \quad (44a)$$

where  $C_a$  and  $G_R$  have been defined earlier in Sec. 2.

The pressure derivative of the polycrystalline shear modulus can be found by analogy to Eq. (36) as

$$(\partial G^{**}/\partial p)_T = (\partial G^{*T}/\partial p)_T = (\partial G^*/\partial p)_T.$$
(45)

or in terms of the single-crystal elastic constants and their pressure derivatives as

$$(\partial G^{*}/\partial p)_{T} = \frac{1}{2} \Big[ \frac{1}{5} + \frac{4}{5} (G_{R}/C_{a})^{2} \Big] (\partial C_{a}/\partial p)_{T} \\ + \frac{3}{10} \Big[ 1 + (G_{R}/c_{44})^{2} \Big] (\partial c_{44}/\partial p)_{T}.$$
(45a)

Specializing  $L^*$  to  $L^{**}$  and  $K^*$  to  $K^{**}$  in Eq. (44), the isothermal pressure derivative of the adiabatic longitudinal modulus is found as

$$(\partial L^{**}/\partial p)_T = (\partial K^{**}/\partial p)_T + \frac{4}{3}(\partial G^*/\partial p)_T.$$
(46)

These quantities  $(\partial G^*/\partial p)_T$  and  $(\partial L^{**}/\partial p)_T$  given by Eqs. (45) and (46), respectively, are the useful quantities for a comparison of the single-crystal acoustic data with polycrystalline acoustic data, since the corresponding quantities can be readily determined from ultrasonic-pressure experiments with polycrystalline specimens.

When we specialize  $L^*$  to  $L^{*T}$  and  $K^*$  to  $K^{*T}$  in Eq. (44), we find that the isothermal pressure derivative of the isothermal longitudinal modulus is

$$(\partial L^{*T}/\partial p)_T = (\partial K^{*T}/\partial p)_T + \frac{4}{3}(\partial G^*/\partial p)_T, \quad (47)$$

where the quantity  $(\partial K^{*T}/\partial p)_T$  has been specified by Eqs. (5) and (31) and the quantity  $(\partial G^*/\partial p)_T$  by Eq. (45a).

By analogy to Eqs. (40) and (42), we obtain the adiabatic pressure derivatives of the adiabatic longitudinal and shear moduli as

$$(\partial L^{*s}/\partial p)_s = C(\partial L^{*s}/\partial T)_p + (\partial L^{*s}/\partial p)_T, \quad (48)$$

and

$$(\partial G^{*s}/\partial p)_s = C(\partial G^{*s}/\partial T)_p + (\partial G^{*s}/\partial p)_T, \quad (49)$$

respectively. The parameter C has been given earlier by Eq. (38), and the quantities  $(\partial L^{*s}/\partial T)_p$  and  $(\partial G^*/\partial T)_p$  can be found from experimental data on the temperature variation of  $c_{up}^{s}$ .

It is important to note that, although the isothermal pressure derivative of the adiabatic shear modulus is exactly the same as that of the isothermal shear modulus, the adiabatic pressure derivative of the adiabatic shear modulus is quite different from the isothermal pressure derivative of the adiabatic shear modulus.

The calculated values of the single-crystal acoustic data corresponding to (a) isothermal pressure derivatives of the isothermal elastic constants and (b) adiabatic pressure derivatives of the adiabatic elastic

		Descitu	611 <sup>8</sup>		6128	644	C.ª	K	$-\left(\partial c_{11}^{s}/\partial T\right)_{p}$	$-\left(\partial \epsilon_{\mathrm{l2}^{8}}/\partial T\right)_{p}$	$-(\partial c_{44}/\partial T)_p$	Reference
Material		(g/cm <sup>3</sup> )	-		0	$\times 10^{-11}  \rm dyn/cm^2)$				<10 <sup>7</sup> dyn/cm <sup>2</sup> -°K	()	(°K)
Al(49Ll)a		2.699	10.5	9	6.39	2.853	4.17	7.78	46.1 <sup>b</sup>	27.2	12.9	298
AI(59SI)		2.697	10.7	3	60.0	2.83	4.64	7.64	46.1 <sup>b</sup>	27.2	12.9	300
Cu(49Ll)		8.941	17.1	0	12.39	7.56	4.71	13.96	40.3°	18.2	25.6	298
Cu(58DI)		8.932	16.8	1	12.14	7.51	4.67	13.70	40.3	18.2	25.6	300
Cu(66HI)		8.932	16.6	1	11.99	7.56	4.62	13.53	40.3°	18.2	25.6	298
a-Fe(66RI		7.872	23.1	4	13.46	11.64	9.68	16.69	39.3 <sup>d</sup>	20.2	9.3	300
MgO(65Bl		3.581	29.7	1	9.54	15.61	20.17	16.26	58.8°	-6.3	12.5	300
<sup>a</sup> This ref <sup>b</sup> G. N. F <sup>e</sup> W. C. O	rence refers to th famm and G. A. verton and J. Gafi	ie author who Alers, J. Ap fney, Phys. F	ose acoustic d ppl. Phys. 35, čev. 98, 969 (	lata have b 327 (196-	xen cited in '4).	Table I.	d J. A • D. F	. Rayne and B. S. I	Chandrasekhar, Phys. G. Lawrence, J. Am. (	Rev. 122, 1714 (1 Ceram. Soc. 47, 44	961). 8 (1964).	

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constants have been already tabulated in Table I. The elastic and thermal properties of each solid used in the construction of Table I are summarized in Tables V and VI. The computed values of polycrystalline acoustic data corresponding to three thermodynamic boundary conditions are illustrated in Table VII with crystalline MgO as an example. In Table VII, also entered are two other values of pressure derivative of the bulk modulus; one is a theoretical value based on the Dugdale-MacDonald relation,12 and the other is derived from the Murnaghan equation of state<sup>13</sup> by a

curve-fitting procedure using experimental compression data.14-17 It is seen here that these values compare very well with the corresponding quantities resulting from the ultrasonic-pressure experiments made on both the single-crystal and polycrystalline materials.

## 5. CALCULATION OF THE POLYCRYSTALLINE ACOUSTIC DATA FROM THE SINGLE-CRYSTAL THIRD-ORDER ELASTIC CONSTANTS

The pressure-dependent second-order elastic constants can be written in a form<sup>11,18</sup>

$$C^{*}_{ijkl}(p) = (\lambda/V^{0}) \left[ \partial^{2} U(V^{0}, S, \tilde{\eta}) / \partial \eta_{ij} \partial \eta_{kl} \right]_{V^{0}, S = \text{const.}, \mathbf{n} = \epsilon \mathbf{1} + p D_{ijkl}$$

$$\tag{50}$$

where

$$D_{ijkl} = \delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk} - \delta_{ik}\delta_{jl}.$$

V denotes the volume of crystal at a reference state characterized by the hydrostatic pressure p, and  $\tilde{\eta}$  is the strain tensor corresponding to an arbitrarily deformed state characterized by that pressure p.  $V^0$  is defined by the relation  $(V/V^0) = \lambda^3$ , where  $\lambda$  is a factor given by the coordinates of a material point in two reference states  $a_i$ and  $a_i^0$  according to  $(a_i/a_i^0) = \lambda$ . The Lagrangian strain tensors<sup>19</sup> corresponding to these two reference states  $\eta_{ii}$ and  $\eta_{ij}^{0}$  are then related by

 $\eta_{ii}^{0} = \lambda^2 \eta_{ii} + \epsilon \delta_{ii}$ 

where  $\epsilon = \frac{1}{2}(\lambda^2 - 1)$ . Keeping in mind the relations  $(\partial/\partial p)_{s,T} = -(V/K^{s,T})(\partial/\partial V)_{s,T}$  and  $(\partial \lambda/\partial V)_0 = (\partial \epsilon/\partial V)_0 = (\partial \epsilon$  $1/3V^{0}$ , one finds by differentiating Eq. (50) that

$$\left(\partial C^{s}_{ijkl}/\partial p\right)_{S} = -\left(1/3K^{s}\right)\left\{\left(1/V^{0}\right)\left[\partial^{2}U(V^{0}, S, \widetilde{\eta})/\partial \eta_{ij}\partial \eta_{kl}\right]_{V^{0}, S=\text{const.}, \mathbf{n}=0}\right\}$$

and

$$\partial C^{s}_{ijkl}/\partial p \rangle_{T} = -(1/3K^{T})((1/V^{0}) [\partial^{2}U(V^{0}, S, \tilde{\eta})/\partial \eta_{ij}\partial \eta_{kl}]_{V^{0}, S=\text{const.}, \mathbf{n}=0}$$

$$+ (1/V^0) \{ (\partial/\partial \eta_{mn}) [\partial^2 U(V^0, S, \tilde{\eta}) / \partial \eta_{ij} \partial \eta_{kl}]_{V^0, S=\text{const.}, \mathbf{n}=0} \} v^0, S=\text{const.}, \mathbf{n}=0 \} + D_{ijkl}.$$
(52)

+  $(1/V_0) [\partial^3 U(V^0, S, \tilde{\eta}) / \partial \eta_{ij} \partial \eta_{kl} \partial \eta_{mn}]_{V^0, S=\text{const.}, n=0} + D_{ijkl},$  (51)

Note that the first terms in Eqs. (51) and (52) are by definition the zero-pressure second-order elastic constants. The second term in Eq. (51) is the zero-pressure third-order elastic constants, whereas that in Eq. (52) is by definition thermodynamically "mixed" third-order elastic constants at p=0. Hence, from these, we obtain the familiar expressions<sup>11</sup>

$$(\partial C^{*}_{ijkl}/\partial p)_{S} = -\left[ (C^{*}_{ijkl} + C^{*}_{ijklmm})/3K^{*} \right] + D_{ijkl}, \tag{53}$$

and

$$(\partial C^{s}_{ijkl}/\partial p)_{T} = -\left[ (C^{s}_{ijkl} + C_{ijklmm})/3K^{T} \right] + D_{ijkl}, \tag{54}$$

where

$$C_{ijklmm} = (1/A) \left\{ C^{s}_{ijklmm} + T\gamma_{G} \left[ -\beta C^{s}_{ijkl} + 3(\partial C^{s}_{ijkl}/\partial T)_{p} \right] \right\}.$$
(55)

Similarly, we find

$$(\partial C^{T}_{ijkl}/\partial p)_{T} = -\left[ (C^{T}_{ijkl} + C^{T}_{ijklmm})/3K^{T} \right] + D_{ijkl}.$$

$$(56)$$

The quantities specified by Eq. (55) are certain linear combinations of the third-order elastic constants  $C_{ijklmn}$ , and they are the primary experimental quantities when ultrasonic-pressure experiments are made with hydrostatic pressure. Thus, for cubic crystals, Cijkimm reduces to the following:

$$C_{I} = C_{111i} = c_{111} + 2c_{112} = -\left[3K^{T}(\partial c_{11}^{s}/\partial p)_{T} + 3K^{T} + c_{11}^{s}\right],$$
(57)

$$C_{II} = C_{1122ii} = 2c_{112} + c_{123} = -\left[3K^T (\partial c_{12}^s / \partial p)_T - 3K^T + c_{12}^s\right],$$
(58)

$$C_{III} = C_{1212ii} = c_{144} + 2c_{166} = -[3K^T(\partial c_{44}/\partial p)_T + 3K^T + c_{44}].$$
(59)

- <sup>12</sup> J. S. Dugdale and D. K. C. MacDonald, Phys. Rev. 89, 832 (1953).
- <sup>13</sup> F. D. Murnaghan, Proc. Am. Acad. Arts Sci. 30, 244 (1944).
   <sup>14</sup> P. W. Bridgman, Proc. Am. Acad. Arts Sci. 67, 345 (1932).
   <sup>15</sup> C. E. Weir, J. Res. Natl. Bur. Std. 56, 187 (1956).

- <sup>16</sup> E. A. Perez-Albuerne and H. G. Drickamer, J. Chem. 43, 1381 (1965).
   <sup>17</sup> R. G. McQueen and S. P. Marsh, to be published in J. Appl. Phys. See also p. 158 of Ref. 8.
- 18 G. Leibfried and W. Lugwig, Solid State Physics, F. Seitz and D. Turnbull, Eds. (Academic Press Inc., New York, 1961), Vol. 12.

<sup>19</sup> F. Birch, Phys. Rev. 71, 809 (1947).

<sup>a</sup> This reference refers to the author whose acoustic data have been cited in Table I. <sup>b</sup> G. N. Kamm and G. A. Alers, J. Appl. Phys. **35**, 327 (1964). <sup>e</sup> W. C. Overton and J. Gaffney, Phys. Rev. **98**, 969 (1955).

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	$-C_{I}$	$-C_{II}$	$-C_{III}$		10 10 (1)	C	(20 (27)
Material	(×	(10 <sup>-12</sup> dyn/cr	m <sup>3</sup> )	 $(\times 10^5 \text{ deg}^{-1})$	$(\frac{\partial \alpha}{\partial I})_p$ (×10 <sup>8</sup> deg <sup>-2</sup> )	$(J/g \cdot deg)$	$(\times 10^3 \text{ J/g} \cdot \text{deg}^{-2})$
Al(49Ll)	22.08	2.43	7.22	2.26ª	1.03	0.903e	0.110
A1(59Sl)	19.48	7.51	7.55	2.26ª	1.03	0.903e	0.110
Cu(49Ll)	27.04	13.60	9.05	1.67 <sup>b</sup>	1.04	0.386°	0.099
Cu(58Dl)	31.09	18.00	14.14	1.67 <sup>b</sup>	1.04	0.386°	0.099
Cu (66Hl)	28.99	16.78	15.63	1.67 <sup>b</sup>	1.04	0.386°	0.099
α-Fe(66Rl)	44.18	21.96	19.17	1.17°	1.02	0.447°	0.418
MgO(65Bl)	50.61	4.60	12.11	1.05 <sup>d</sup>	1.75	0.916 <sup>f</sup>	1.80

TABLE VI. Acoustic and thermal data for crystalline Al, Cu,  $\alpha$ -Fe, and MgO ( $\sim$ 300°K).

<sup>a</sup> D. F. Gibbon, Phys. Rev. 112, 136 (1958).

<sup>b</sup> D. Bijl and H. Pullan, Physica 21, 285 (1955).

<sup>e</sup> F. C. Nix and D. MacNair, Phys. Rev. 60, 597 (1941).

<sup>d</sup> J. G. Collins and G. K. White, Progress in Low-Temperature Physics C.J. Gorter, Ed. (North Holland Publishing Co., Amsterdam, 1964), p. 450.

Where  $c_{\mu\nu\lambda}$  are the "mixed" third-order elastic constants in Voigt's notation. Once the values of  $(\partial c_{\mu\nu}{}^{s}/\partial p)_{T}$  are found from these Eqs. (57) through (59), the calculations of polycrystalline acoustic data follow the procedure given in the previous sections.

## 6. DISCUSSION AND IMPLICATIONS OF THE PRESENT WORK

(a) The theoretical scheme of calculating the isotropic pressure derivatives of isotropic elastic moduli has been presented for cubic, hexagonal, trigonal, and tetragonal crystals. The scheme has been successfully tested for four cubic solids and also for one hexagonal metal of which both single-crystal and polycrystalline acoustic data are available. Although further testings of this scheme are needed, the writer believes that the validity of the present theoretical scheme is essentially established for cubic and hexagonal crystals; it is also believed that the scheme will probably apply for crystals of the lower symmetry.

For further testing of the validity of the scheme, the followings may be suggested: It would be of particular interest to test this scheme for highly anisotropic cubic crystals like RbI and Li as well as moderately anisotropic crystals like KCl and LiF, so that one may find to what extent the scheme is applicable for crystals of high elastic anisotropy. Also interesting work would be to test the scheme for rather incompressible solids like  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiC as well as for rather compressible materials like K and Na. The work of this kind would probably provide important information concerning the effects of grain boundaries on the polycrystalline acoustic data and on the compression behavior of aggregate solids like rocks.

(b) The thermodynamic relations are presented (in terms of the measured isothermal pressure derivatives of adiabatic elastic moduli) for the isothermal pressure derivatives of the isothermal elastic moduli, and also <sup>e</sup> Landolt-Börnstein Tables, 6th ed. (Springer-Verlag, Berlin 1961), Vol. 2 (Pt. 4).

<sup>1</sup> T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) A250, 70 (1959).

for the adiabatic pressure derivatives of the adiabatic elastic moduli. The acoustic data obtained from the usual ultrasonic-pressure experiments are the isothermal pressure derivatives of adiabatic elastic moduli; they are, for example, the practical quantities in the study of the propagation of seismic waves in the interior of the earth. The isothermal pressure derivatives of the isothermal elastic moduli are the quantities usually resulting from theoretical calculations according to the lattice theory of solids, and thus, they have important applications in testing of a theory with experimental values. In addition, these quantities have a direct application in the study of the compression in the earth interior. The adiabatic pressure derivatives of the adiabatic elastic moduli arise directly from the shock-wave experiments, and the calculated values corresponding to this thermodynamic boundary condition are useful in the study of the actual shock-wave propagation.

(c) In the following, two possible applications of the theoretical scheme are indicated: One is that the isotropic values  $dL^*/dp$  and  $dG^*/dp$  can be used in the calculation of the acoustic Grüneisen constant, in place

TABLE VII. Pressure derivatives of polycrystalline elastic moduli at different thermodynamic boundary conditions ( $\sim$ 300°K).

Pressure derivatives	$dK^*/dp$	dG*/dp	$dL^*/dp$
$(\partial M^* / \partial p)_T$	4.14ª 4.12 <sup>b</sup>	2.47ª	7.43*
$(\partial M^T / \partial p)_T$	4.18 4.00(±0.07)°	2.47	7.47
$(\partial M^{s}/\partial p)_{s}$	4.10	2.41	7.32

<sup>a</sup> Values taken from Table II.

mental compression data.

<sup>b</sup> Value obtained from the Dugdale-MacDonald relation; i.e.,  $[(\partial K^{\theta}/\partial p)T]_{p=0} = 2\gamma_G + 1$ , where  $\gamma_G$  is the Grüneisen parameter. <sup>6</sup> Value obtained from the Murnaghan equation of state using experiU

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 $(\partial C_p / \partial T)_p$ (×10<sup>3</sup> J/g·deg<sup>-2</sup>) 0.110 0.110 0.099 0.099 0.099 0.418 1.80

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of the adiabatic tained from the re the isothermal ic moduli; they ies in the study n the interior of erivatives of the antities usually according to the have important th experimental have a direct sion in the earth tives of the adithe shock-wave es corresponding lition are useful propagation. plications of the

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lline elastic moduli tions (~300°K).

/dp		dL*/dp	
17ª	*	7.43ª	
17		7.47	
11		7.32	
and the second s			

onald relation; i.e., n parameter. f state using experiof  $dc_{\mu\nu}/dp$ . In such a case, the calculation of the acoustic Grüneisen constant is simplified and easily tractable in the procedure; it gives "mean" Grüneisen's mode gammas (longitudinal and transverse). The detail of this subject will constitute a topic of a later publication.

Another important use of the theoretical scheme is that, for anisotropic noncubic solids, the values of  $K_0^*$ and  $[(dK^*/dp)_T]_{p=0}$  calculated from single-crystal acoustic data should be used as the constants in the Murnaghan equation of state. Although a subsequent communication will discuss this subject in some detail, it is noted here that the use of the usual  $K_R$  and its first pressure derivative at p=0 as the Murnaghan constants is inaccurate procedure.20

(d) In conclusion, the present work suggests an important implication that the acoustic data measured on *fully dense* polycrystalline specimens may be as

20 (unpublished).

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useful as their single-crystal acoustic data in the study of the equation of state of solids, for example. And further, when anisotropic single-crystal acoustic data are available, these can be converted into isotropic polvcrystalline acoustic data so that in their applications the use of the acoustic data becomes more practical.

#### ACKNOWLEDGMENTS

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Temperature Effects on Several Fluorescence Pair Lines in Ruby

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The widths and positions of several lines in the fluorescence spectrum of ruby with 0.94 at.% Cr<sup>3+</sup> belonging to the second  $(N_1)$  and the fourth  $(N_2)$  nearest neighbor pair systems have been measured between 20° and 270°K. The linewidths are explained in terms of microscopic strains, Raman scattering of phonons, and direct phonon processes. The lineshifts with temperature are due to the absorption and emission of virtual phonons, and are approximately the same for all the lines investigated. A Debye model of phonons was used with different effective Debye temperatures for linewidth and lineshift processes.

We have investigated the temperature dependence of the widths and positions of several lines in the fluorescence spectrum of ruby, with 0.94 at. % Cr3+, belonging to the second nearest neighbor  $(N_1)$  and fourth nearest neighbor  $(N_2)$  pair systems<sup>1</sup> in order to compare the effects of strains and various phonon processes on different transitions within the same pair system. These measurements were done in the temperature range from 20° to 270°K, and the results are compared with those obtained previously for different lines on the same sample.<sup>2</sup> The lines investigated are due to the transitions shown in Fig. 1, and at 70°K

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<sup>1</sup> P. Kisliuk, A. L. Schawlow, and M. D. Sturge, in Quantum *Electronics*, P. Grivet and B. Bloembergen, Eds. (Columbia University Press, New York, 1964), Vol. I, p. 725. <sup>2</sup> R. C. Powell, B. DiBartolo, B. Birang, and C. S. Naiman, J.

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appear at 6948.6, 7058.2, 6987.7, 6989.4, and 7001.8 Å.<sup>3</sup> The first two lines belong to the same pair system as the  $N_1$  (7040.6-Å) line, the latter three to the same pair system as the  $N_2$  (7008.8-Å) line.

The details of the experimental apparatus have been described in a previous paper.<sup>2</sup> For these measurements a McPherson model 213 1-m monochromator was used in first order with a slit width of 20  $\mu$  to achieve a resolution of  $0.60 \text{ cm}^{-1}$ .

The experimental results and the theoretical fittings of the thermal variation of the fluorescence widths of the lines investigated are shown in Fig. 2. The curves for the linewidths are similar to each other and to those of the  $N_1$  and  $N_2$  lines in that they are constant up to about 80°K and then increase rapidly

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<sup>&</sup>lt;sup>3</sup> R. C. Powell, B. DiBartolo, B. Birang, and C. S. Naiman Phys. Rev. 155, 296 (1967).